

## PATENT ABSTRACTS OF JAPAN

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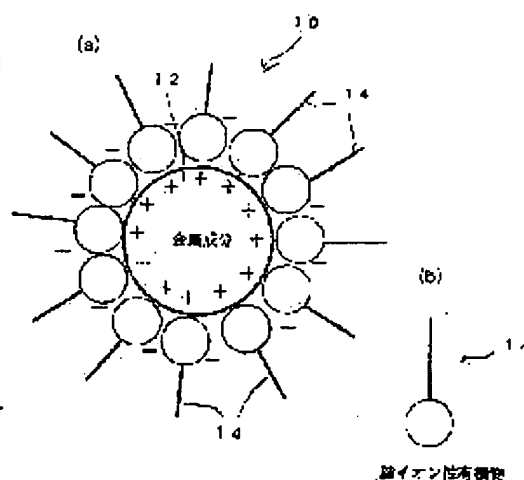
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## (54) COMPOSITE METALLIC SUPERFINE GRAIN AND ITS MANUFACTURING METHOD

## (57)Abstract:

PROBLEM TO BE SOLVED: To provide a composite metallic superfine grain uniform in diameter, excellent in dispersion stability and property stability as the grain and capable of being manufactured on an industrial scale and its manufacturing method.

SOLUTION: A positively charged cationic core metal 12 having 1-20 nm diameter is surrounded by an anionic organic material 14 to constitute the composite metallic superfine grain, and the grain is manufactured by heating a low-temperature decomposable low-molecular-weight organometallic salt, such as a metallic salt, e.g. a carbonate, a formate or an acetate, in a non-aqueous solvent in the presence of the anionic organic material above the decomposition temperature of the metallic salt and below the decomposition temperature of the anionic organic material.



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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

[Field of the Invention] This invention relates to the compound ultra-fine particle starts a compound ultra-fine particle and its manufacture approach, especially is excellent in distributed stability, and it enabled it to manufacture on a scale of industrial, and its manufacture approach.

**[0002]**

[Description of the Prior Art] Particle diameter makes a metaled ultrafine particle solidify out of a gaseous phase by evaporating a metal under existence of some gas among a vacuum as the manufacture approach of an ultra-fine particle 100nm or less, and, generally what obtained the overly detailed metal particle is known. However, since equipments, such as an electron beam, BURAZUMA, laser, and induction heating, are need in order are not fit for mass production method and to evaporate a metal, since there are few a uniform metal membrane's not being obtained and amounts of generation of an ultra-fine particle in order that a grain boundary may remain, even if it is large with [ of particle size distribution ] \*\* and they heat-treat by the approach using such a physical process, cost will become high.

[0003] Moreover, although it had to use dispersedly into the solvent using the surfactant etc. since it would condense if it takes out in air independently when using such an ultra-fine particle, the shelf life of the field of distributed stability etc. was inadequate.

[0004] By for this reason, the thing heated under the inert gas ambient atmosphere which intercepted oxygen using an organic metal compound at the temperature of beyond the decomposition initiation temperature of that organic metal compound, and under perfect decomposition temperature Although the ultra-fine particle by which the surroundings of it are enclosed with the organic compound by mainly consisting of metal components originating in the organic metal compound concerned, and the core consisting of a metal component substantially, and its manufacture approach are proposed A special ambient atmosphere is needed, and decomposition temperature is high, and it can use only in a specific field.

**[0005]**

[Problem(s) to be Solved by the Invention] If it is in an ultra-fine particle and is made to gather in the state of a particle with nakedness, particles will adhere easily and condensation and the shape-ization of a chain will take place. For this reason, in order to stabilize an ultra-fine particle in the condition of having detached mutually, it is necessary to form a certain protective film in the front face of a metal particle. Until now, it was thought that an ultra-fine particle was neutrality electrically, and, for this reason, generally, nonionic matter, such as a nonionic surfactant or gelatin, and polyvinyl alcohol, was used as said protective film.

[0006] Even if this is in the ultra-fine particle surrounded with the organic metal compound on which said core is a metal component and the surroundings of it function as a protective film, it is the same, and this core metal component and organic metal compound are considered to have joined together with intermolecular affinities, such as Van der Waals force.

[0007] However, also in metal concentration with a for example more high ultra-fine particle, in order to be stable as a particle, it is desirable for the main metal section and the protective film around it to have not an intermolecular affinity with comparatively small energy but a certain powerful bonding strength.

[0008] Artificers found out that an ultra-fine particle with cation nature was formed in the process which pyrolyzes a certain kind of metal salt. Therefore, if the anionic organic substance which forms a desirable protective film exists when an ultra-fine particle with cation nature is formed, on the surface of an ultra-fine particle, the anionic organic substance etc. will carry out ionic bond stably, and will become a compound ultra-fine particle in the condition that the stable protective film was formed.

[0009] that which succeeded in this invention in view of the above-mentioned situation -- it is -- particle diameter -- more -- uniform -- as distributed stability and a particle -- description -- it excels in stability and aims at offering the compound ultra-fine particle it enabled it to manufacture on a scale of industrial, and its manufacture approach.

[0010]

[Means for Solving the Problem] Invention according to claim 1 is a compound ultra-fine particle with the structure which surrounded the perimeter of the just charged core metal with a diameter of 1-20nm by many anion matter.

[0011] Although it is known that the melting point of metal particles will fall if particle size becomes small, it is 20nm or less that the effectiveness appears, and the effectiveness will become remarkable if set to 10nm or less. Therefore, as for the mean particle diameter of a core metal (ultra-fine particle), it is desirable that it is 1-20nm, and it is desirable that it is especially 1-10nm. moreover, ionic bond of a core metal and the anion matter is carried out firmly, and the distributed stability in a solvent is improved by making a role of a protective film which protects a core metal to the anion matter play -- making -- moreover -- the description as a particle -- stability can be raised.

[0012] Invention according to claim 2 is a compound ultra-fine particle according to claim 1 characterized by the metal component of said core metal being at least one sort of Cu, Ag, Au, In, Si, Ti, germanium, Sn, Fe, Co, nickel, Ru, Rh, Pd, Os, Ir, Pt, V, Cr, and Bi.

[0013] Invention according to claim 3 is a compound ultra-fine particle according to claim 1 or 2 characterized by said anion matter being the ionicity organic substance. Invention according to claim 4 is a compound ultra-fine particle according to claim 3 characterized by said ionicity organic substance being a with a carbon numbers of five or more fatty acid, alkylbenzene sulfonic acid, or alkyl sulfonic acid.

[0014] Invention according to claim 5 is among a nonaqueous solvent, and is the manufacture approach of the compound ultra-fine particle characterized by the metal salt and being more than the decomposition reduced temperature of this metal salt, and heating the low-molecular-weight organic metal salt of low-temperature resolvability, such as a carbonate, formate, or acetate, below with the decomposition temperature of said ionicity organic substance more preferably under existence of the ionicity organic substance. Without using large-scale vacuum devices, since it is producible in the chemical process in the inside of the liquid phase, such a compound ultra-fine particle can be mass-produced under the usual atmospheric-air ambient atmosphere using easy equipment, and its cost is cheap. And since particle size is uniform, all particles will weld with constant temperature.

[0015]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained with reference to a drawing. Drawing 1 shows typically the structure of the compound ultra-fine particle of the gestalt of operation of this invention, and this compound ultra-fine particle 10 consists of a core metal 12 charged in forward [ which consists of a metal component substantially ], and the ionicity organic substance 14 as anion matter which encloses the perimeter of this core metal 12. That is, this compound ultra-fine particle 10 consists of a metal salt which are the organic anionic matter and starting material, for example, a carbonate, formate, or a metal component of the acetate origin, that core consists of a core metal 12, and the ionicity organic substance 14 encloses the surroundings of it.

[0016] This ionicity organic substance 14 has the small inclination condensed in a solvent by playing a role of a protective film of the core metal 12, and covering the perimeter of the core metal 12 with the

ionically organic substance 14 in this way, and the compound ultra-fine particle 10 excellent in distributed stability is constituted. and the conventional ultra-fine particle stabilized by existing after the part or all has combined firmly the ionically organic substance 14 and the core metal 12 by ionic bond, and carrying out coating by the surface active agent -- differing -- the description as a particle -- while it is extremely stable, also in higher metal concentration, it is stable.

[0017] Although it is good, about 50 - 90 % of the weight, then especially when using for the pad metallic material of a wiring gutter, for example, it is usually desirable [ the ratio of the core metal 12 in this compound ultra-fine particle 10 ] to consider as 70 - 90 % of the weight about 60 to 90% of the weight.

[0018] About 1-20nm of mean particle diameter of the core metal 12 of said compound ultra-fine particle 10 is usually about 1-10nm preferably. Although falling if particle size becomes small is known, it is 20nm or less that the effectiveness appears, and if the melting point of metal particles is set to 10nm or less, it will become remarkable [ the effectiveness ]. Therefore, it becomes possible by constituting in this way to carry out melting of the core metal 12 of the compound ultra-fine particle 10 below with the melting point of metal original. For example, if it is in silver, the melting point is 1233K (960 degrees C), but if it is a silver ultrafine particle with a particle diameter of 5nm, silver fuses at about 220 degrees C.

[0019] The coat which consists only of fused silver can be formed by using a silver ultrafine particle with a particle size of 5nm, and heating to the decomposition temperature of the ionically organic substance 14 as a core metal 12, by this, at 220 degrees C with it [ more than ], if it is in the compound ultra-fine particle which enclosed and constituted this perimeter from the ionically organic substance 14, and the decomposition temperature of this ionically organic substance 14 is 220 degrees C or less.

[0020] Said compound ultra-fine particle 10 is for example, among a nonaqueous solvent, is more than the decomposition reduced temperature about a metal salt, for example, a carbonate, formate, or acetate under existence of the ionically organic substance, and can be manufactured by heating below with the decomposition temperature of the ionically organic substance.

[0021] As a metal component of said core metal 12, at least one sort of Cu, Ag, Au, In, Si, Ti, germanium, Sn, Fe, Co, nickel, Ru, Rh, Pd, Os, Ir, Pt, V, Cr, and Bi is used, and a with a carbon numbers of five or more fatty acid, alkylbenzene sulfonic acid, or alkyl sulfonic acid is used as the ionically organic substance.

[0022] Whenever [ stoving temperature ] is more than the decomposition reduced temperature of a metal salt, for example, a carbonate, formate, or acetate, and is below the decomposition temperature of the ionically organic substance. For example, what is necessary is just to hold to the temperature which 200 degrees C or more and the above-mentioned ionically organic substance do not decompose, since there are 200 degrees C of the decomposition initiation temperature in the case of silver acetate. In this case, in order to make it be hard to disassemble the ionically organic substance, although it is desirable that it is an inert gas ambient atmosphere as for a heating ambient atmosphere, it can be heated under atmospheric air by selection of a nonaqueous solvent.

[0023] After heating is completed, it refines according to a well-known purification method. What is necessary is for centrifugal separation, film purification, solvent extraction, etc. just to perform a purification method.

[0024] Thus, compound ultra-fine particle dispersion liquid are produced by distributing the produced compound ultra-fine particle 10 in suitable organic solvents, such as a cyclohexane. Since the particulate material is dramatically fine, where a compound ultra-fine particle is mixed and stirred, such compound ultra-fine particle dispersion liquid are almost transparent, and can adjust physical-properties values, such as surface tension and viscosity, by choosing the class of solvent, ultrafine particle concentration, temperature, etc. suitably.

[0025]

[Example 1] Silver acetate was used as a source of a metal, using oleic acid as organic anionic matter. Naphthene [ of 250 degree C of \*\*\*\* ] high-boiling point solvent 0.5L was put into the eggplant mold flask of volume 1L, 10g of silver acetate and 20g of oleic acid were put in into it, and it heated at 240

degrees C for 3 hours. According to heating, the color tone changed to light brown color and a pan purple from colorlessness. The acetone was added after heating and precipitate purification was performed.

[0026] When this denatured powder was observed with the transmission electron microscope, particle size consisted of ultrafine particles which are about 10nm. Furthermore, when the powder X diffraction was performed, the core of metal silver was checked.

[0027] When toluene and a xylene were made to distribute the powder which consists of this compound ultra-fine particle, precipitate was accepted by neither of the cases but changed into the transparent condition at them. That is, having been in a solubilization condition was admitted.

[0028] After having applied by having made this into compound ultra-fine particle dispersion liquid so that it might be set to 0.05g per two 1cm on the surface of a base material, and drying, it heated at about 250 degrees C under nitrogen-gas-atmosphere mind. Then, it calcinated easily and the silver coating film was formed.

[0029]

[Example 2] Copper carbonate was used as a source of a metal, using stearic acid as organic anionic matter. Paraffin series [ of 250 degree C of \*\*\*\* ] high-boiling point solvent 0.5L was put into the eggplant mold flask of volume 1L, 10g of copper carbonate and 40g of stearic acid were put in into it, and it heated at 300 degrees C for 3 hours. According to heating, the color tone changed to a dark green one and a pan brown from the light green color. The methanol was added after heating and precipitate purification was performed.

[0030] This compound ultra-fine particle was applied to the base material by the same approach as an example 1. However, heat-treatment temperature was made into 300 degrees C. Then, it calcinated easily and the copper coating film was formed.

[0031]

[Example 3] Chloroplatinic acid was used as a source of a metal, using sodium dodecyl benzenesulfonate as organic anionic matter. Xylene (isomer mixing article) 0.5L was put into the eggplant mold flask of volume 1L, 5g of chloroplatinic acid and 20g of sodium dodecyl benzenesulfonate were put in into it, and it heated at 150 degrees C for 3 hours. According to heating, the color tone changed to light brown color and a pan from yellow at gray. The acetone was added after heating and precipitate purification was performed.

[0032] This compound ultra-fine particle was applied to the base material by the same approach as an example 1. However, heat-treatment temperature was made into 200 degrees C. Then, it calcinated easily and the platinum coating film was formed.

[0033]

[Effect of the Invention] By making a role of a protective film which is made to carry out ionic bond of the core metal and anion matter whose mean particle diameter is 1-20nm firmly, and protects a core metal to the anion matter play, as explained above according to this invention the distributed stability in a solvent -- excelling -- moreover -- the description as a particle -- even after raising stability, being easy to carry out handling and dispersing a solvent, chemical stability can be maintained until it is decomposed thermally and production control can offer an easy compound ultra-fine particle. And without using large-scale vacuum devices, since it is producible in the chemical process in the inside of the liquid phase, it can mass-produce under the usual atmospheric-air ambient atmosphere using easy equipment, and cost is cheap. And since particle size is uniform, all particles will weld with constant temperature.

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CLAIMS

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[Claim(s)]

[Claim 1] A compound ultra-fine particle with the structure which surrounded the perimeter of the just charged core metal with a diameter of 1-20nm by the anion matter.

[Claim 2] The metal component of said core metal is a compound ultra-fine particle according to claim 1 characterized by being at least one sort of Cu, Ag, Au, In, Si, Ti, germanium, Sn, Fe, Co, nickel, Ru, Rh, Pd, Os, Ir, Pt, V, Cr, and Bi.

[Claim 3] Said anion matter is a compound ultra-fine particle according to claim 1 or 2 characterized by being the ionicity organic substance.

[Claim 4] Said ionicity organic substance is a compound ultra-fine particle according to claim 3 characterized by being a with a carbon numbers of five or more fatty acid, alkylbenzene sulfonic acid, or alkyl sulfonic acid.

[Claim 5] The manufacture approach of the compound ultra-fine particle which is among a nonaqueous solvent, is more than the decomposition reduced temperature of this metal salt about a metal salt under existence of the ionicity organic substance, and is characterized by heating below with the decomposition temperature of said ionicity organic substance.

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[Translation done.]